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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

This program applied the technique of Surface Enhanced Raman Scattering to study the decomposition of organophosphonates on metal surfaces (micro-structures) towards the goal of effective decontamination. Reaction kinetics were studied, the product distributions were observed. Outgrowths of this research are studies of corrosion and passivation of Ag by the reactions of the oxyanions CrO_4^{2-} and MnO_4^{2-} in electrochemical cells which resulted from research into the adsorption properties of protonated phosphates.

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REPORT 9

SURFACE ENHANCED RAMAN MEASUREMENT OF THE OXIDATION
REACTIONS OF GASES ON METAL SURFACES

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A. The Research Results

The focus of the research, carried out under funding from Contract N00014-85-K-01050, was to examine the ability of metal surfaces, principally Ag metal, to catalyze the decomposition of phosphonates. The development of Surface Enhanced Raman Scattering (SERS) in the early 1980's indicated that it would be an effective probe of surface chemical reactions since the SERS effect on Ag metal microstructures was shown to be sensitive to less than monolayer coverage of the surface.

Simultaneous with the discovery of SERS, new multichannel linear diode array detectors were being developed which, when used with microchannel plates, facilitated a Raman instrumental system extraordinarily effective in reducing scan times (integration time) from over 30 minutes to less than 1s. Thus, this instrument was a very powerful probe of quasi real-time surface kinetics.

Given the state of these developments, the surface decomposition of phosphonates (dimethyl-methyl, diethyl-ethyl, dibutyl-butyl and dihexyl-hexyl phosphonate) was examined at room temperature. Despite preliminary data to the contrary, only a slow decomposition of any of these species was observed. Yet it was well documented that clean Ag metal surfaces exposed to O_2 gas formed a very strongly basic surface which was capable of abstracting H even from $-CH_3$ groups in many organic compounds. The apparent slowness of the reactions with phosphonate was postulated to be due to the lack of clean oxide covered surfaces with Ag metal substrate which had SERS active and catalytically active Ag microstructures.

A program was embarked upon to generate chemically, a matrix of fresh Ag microstructures (Technical Report 1) by reacting NO_2/N_2O_4 gas with Ag metal powders. The initially formed surface of $AgNO_2$ autocatalytically decomposed to make $AgNO_3$, NO and Ag_n , where Ag_n represents Ag microstructures which are extremely reactive chemically, (Technical Reports 5 and 6). With acidic organic gaseous compounds such as C_2H_2 and $CH_3C\equiv CH$, the decomposition reactions are extremely rapid even at room temperature with both compounds suffering hydrogen abstraction and the formation of an overlayer of graphitic carbon on the Ag metal surface. Subsequent pulses of the acetylene do not cause much change because this overlayer prevents contact with the Ag.

The reactive matrix of Ag microstructures imbedded in $AgNO_3$ is less effective in destroying phosphonates. Nevertheless, the reactions are quite similar in that the end products are graphitic carbon and some adhered $-CH$ fragments as evidenced by a peak at $\sim 3000cm^{-1}$. The carbon overlayer is removeable only with extensive heating, (Technical Report 7). In any event, the use of Ag metal microstructures to cause decomposition of phosphonates is ineffective, not because of the lack of initial reactivity, but because of the rapid formation of a non-reactive C overlayer.

One of the unknowns in the decomposition of phosphonates on Ag metal is the fate of the P-containing fragments. It was presumed that phosphates would be evidenced, but no SERS spectrum was observed containing peaks that could be identified as protonated phosphates. Nevertheless, this research effort has led



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to several very exciting and important chemical results which occur with tetrahedral oxyanions adsorbed on Ag metal surfaces.

Initially, $\text{CrO}_4^{=}$ was used in place of phosphate ions in a study of adsorption on a Ag metal electrode in an electrolytic solution. After an initial oxidation-reduction cycle using standard voltammetry techniques, a broad peak at about 570 cm^{-1} was observed during a cathodic (negative sweep). Since this peak was not due to adsorbed $\text{CrO}_4^{=}$, we decided to use other oxidants to identify this strong peak. Upon replacement of $\text{CrO}_4^{=}$ with MnO_4^- in micromolar quantities, a similar peak was observed. During the cathodic sweep additional successive SERS peaks were observed which could be identified on adsorbed oxide ($\sim 600\text{ cm}^{-1}$), hydroxide ($\sim 500\text{ cm}^{-1}$), water ($\sim 400\text{ cm}^{-1}$) and a water polymer ($\sim 460\text{ cm}^{-1}$). Thus, for the first time, the protonation of a surface oxide layer to form adsorbed OH^- , H_2O and H_3O_2^+ was observed in a reversible sequence of steps. (Technical Reports 2,3,8).

These results are extremely promising as affording a route to the direct elucidation of the electrochemical processes of corrosion and passivation. For instance, if O_2 gas is added to an electrolytic solution containing MnO_4^- and a Ag electrode biased at a voltage at which H_2O is adsorbed on the surface, the hydrogen atoms are observed to be removed one at a time until the surface is covered with a oxide layer (Technical Report 3). This process is completely reversible. In contrast, $\text{CrO}_4^{=}$ containing electrolytes form only adsorbed hydroxide on Ag metal surfaces. This hydroxide may be deprotonated with O_2 gas also (Technical Report 8). Since a common passivation technique for metals is to treat them with $\text{CrO}_4^{=}$ solutions, it seems clear that the passivation process is related to the inability of $\text{CrO}_4^{=}$ treated surfaces to protonate completely to form a H_2O covered surface. Future work will be necessary to examine these and other systems to determine the mechanisms of proton and electron transfer on Ag and other metals.

It is well known that metal surface potentials may be modified by the incorporation of impurity ions, especially the alkalis. In catalysis, the efficacy is evidenced by either poisoning or enhancing the reaction kinetics. In corrosion, the effects are apparent from the rate of chemical reaction. Spectroscopically, the effects are observed by a modification of adsorbates vibrational frequencies or by the formation of other chemical adsorbates. We have shown that the latter is prevalent in Mg^{+2} containing solutions of a MnO_4^- electrolyte. In this case, the Mg^{+2} incorporated into the surface modifies the surface so that hydroxides ions adsorbed on the surface are observed which differ in their spatial distribution. (Technical Report 4) Presumably, rates of metal corrosion can be modified by impurity implantation techniques which modify the surface potentials in a yet to be determined manner.

B. Technical Reports

1. (U) The Reactions of $\text{NO}_2/\text{N}_2\text{O}_4$ with Ag: A Surface Enhanced Raman Scattering and Ellipsometric Measurement.
2. (U) The Observation with Surface-Enhanced Raman Scattering of the Sequential Electrochemical Formation of Adsorbed O_2^- , OH^- , and H_2O on a Ag Electrode.

3. (U) Molecular Precursors to the formation of H_2 and the Reduction of O_2 at Ag Cathode: A Surface-Enhanced Raman Scattering Experiment.
4. (U) Surface Enhanced Raman Scattering from OH^- Absorbed on a Ag Electrode in Dilute Mg^{+2} Electrolytes.
5. (U) The Reactons of C_2H_2 and CH_3C_2H on Ag Powder
6. (U) The Application of SERS to Study Surface Oxidation Reactions of Phosphonates.
7. (U) Surface Enhanced Raman Scattering Applied to Surface Chemical Kinetics.
8. (U) The Formation of Adsorbed O^{2-} , and OH^- on a Ag Electrode in Dilute $CrO_4^{=}$ Electrolytes.

C. Journal Articles

1. "The Observation with Surface Enhanced Raman Scattering of the Sequential Electrochemical Formation of Adsorbed O^{2-} , OH^- , and H_2O on a Ag Electrode," J. Phys. Chem. 90, 5808 (1986)
2. "The Molecular Precursors to the Formation of H_2 and the Reduction of O_2 on a Ag Electrode: A Surface Enhanced Raman Scattering Experiment," J. Phys. Chem. 90, 5812 (1986)
3. "The Reactons of NO_2/N_2O_4 with Ag: A Surface Enhanced Raman Scattering and Ellipsometric Measurement" with Joseph E. Boggio, J. Chem. Phy. 84, 135 (1986)
4. "The Formation of Adsorbed OH^- on Ag Electrodes in Dilute Electrolytes Containing $KMnO_4$ ", J. Phys. Chem., 92, 2546 (1988)
5. "The Protonation of Adsorbed Vanadates on Ag Electrodes", with E.A. Dinces In preparation.
6. "The Formation of Adsorbed O^{2-} and OH^- on a Ag Electrode in Dilute $CrO_4^{=}$ Electrolytes". Submitted to Langmuir.
7. "The Reactions of Propyne and Acetylene on Ag Powders: A SERS Experiment", with J. Boggio, Mater. Res. Soc., Nov, 1987

D. Thesis

The Protonation of Vanadate Species Adsorbed onto Silver Electrodes:
A Surface Enhanced Raman Scattering Study, Elizabeth A. Dinces, Amherst
College, Amherst, MA 01002, 1987

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